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Diamond like coating and a method of forming the same.

A method of depositing diamond-like films produces depositing species from a plasma of a hydrocarbon gas precursor. The plasma is generated by a laser pulse which is fired into the gas and is absorbed in an initiator mixed with the gas. The resulting detonation produces a plasma of ions, radicals, molecular fragments and electrons which is propelled by the detonation pressure wave to a substrate and deposited thereon.

EP 0 384 772 A1

DIAMOND LIKE COATING AND A METHOD OF FORMING THE SAME

Diamond-like coatings are in great demand for many purposes, for example: as protective coatings for optical and other components; as coatings in sliding wear parts such as valves, pistons or bearings; as heat sinking materials in integrated circuit technology; and as laser host material. Diamond-like coatings also have great potential as an integrated circuit semi-conductor material because of the very high heat transfer of such materials. By "diamond-like coatings", we mean, as is common in the art, coatings formed of carbonaceous species having characteristics of hardness and chemical structure similar to natural diamond, at least in part. Such coatings may include other species of chemicals and structure, at least in part, and/or may include species more similar to or closely resembling natural diamond.

Because of the great demand for these materials, various techniques have been developed to produce them. Common to all of the known production techniques is the formation of a gas plasma, which acts as a source of the free radicals and ions forming the depositing species and/or coating environment and which provides the transient energy required for diamond or diamond-like film nucleation. Conventional methods require radio frequency electronics to generate the plasma and, moreover, require suitable filtering and collimating electrodes to extract and control the depositing species.

In addition, conventional methods require the provision of means for ensuring an electrical potential difference between the plasma region and the substrate to be coated, normally in the range of from 100 to 1,000 electron volts potential difference. A further problem common to conventional methods of formation of diamond-like coatings is the requirement that adequate cooling be provided for the substrate, since the substrate is necessarily in close proximity to a very hot plasma. Conventional processes require that the substrate be maintained near room temperature as a key ingredient to forming diamond-like coatings. Heating of the coating films, either during formation or afterwards, will collapse the sp³ bonding characteristic of diamond films to an sp² bonding, that is, will convert the diamond-like film to one of graphite.

Diamond-like coatings formed by state of the art methods notoriously have problems with adhesion to the substrate and are unable to support a shear stress. The industry recognizes a ten μm thickness limit as that which is attainable by conventional processes. The accumulation of diamond-like material above this limit incurs problems with the cohesive forces within the film, and this in-

duces delamination of the film. Moreover, attempts to produce film beyond the ten μm thickness result in the collapsing of the sp³ hybrid to the sp² bonding, that is, the formation of graphite. These films, above the ten μm thickness, have a very weak bond to the substrate such that the diamond-like coating can be easily scraped from the substrate, for example by application of a dental pick.

Conventional plasma-assisted techniques for producing diamond-like coatings grow coatings which have separate, granular crystal structure, that is, an irregular geode-like appearance on microscopic examination. These films of discrete crystalline nature are particularly unsatisfactory when used as optical coatings since scattering of light as a result of the separate crystals can degrade the optical throughput.

With the process of the present invention, continuous, tightly adhering, optically suitable diamond-like films may be deposited on substrates such as lenses, or on other surfaces subject to wear, without the use of the electronics and electrodes necessary in state of the art deposition processes.

In accordance with the present invention, there is provided a substrate having a hard diamond-like coating thereon, the diamond-like coating being tightly bonded to the substrate and containing fluorocarbon moieties.

The invention also provides a method of producing a diamond-like coating, which comprises introducing a laser generated beam into a confined hydrocarbon-containing precursor gas to initiate a plasma in the precursor gas and create diamond-like precursor fragments from the precursor gas, the plasma propelling the fragments onto a substrate and bonding the fragments to the substrate as a diamond-like coating.

Thus, the process of the present invention generates a plasma by the absorption of laser radiation into a precursor gas or gas mixture. The gas rapidly decomposes to produce the accelerating forces and the depositing species necessary to produce diamond-like coatings. Externally generated accelerating fields or potentials between the gas and the substrate are not required. Moreover, it is not necessary to heat the substrate substantially prior to deposition. Instead, the plasma region may be spaced from the substrate and generated intermittently, for example at ten microseconds duration, so that the temperature excursions are transient and high energies are developed to propel the deposition species onto the substrate. This system does not require a sophisticated vacuum system, as do conventional methods, since the

coatings may be produced at atmospheric pressure as well as at reduced pressure. For example, the process of the present invention may typically operate at from one to 100 torr (1.33 to 133×10^{-3} bar) total pressure. Conventional deposition processes normally take place at millitorr pressures.

The process of the present invention may also work to provide deposition coverage of substantially greater areas than can previous techniques. Previously, the art required collimated beams or very localized plasma mixtures, which result in small area coverage. The process of the present invention may be used over much wider areas. Moreover, the films produced by the process of the present invention may be much thicker than are conventional films. We have produced films of greater than ten μm thickness. At this thickness the films produced by the process of the present invention have a very high adhesion to the substrate. Standard pull tests indicate that the films produced by the process of the present invention may withstand in excess of 10,000 psi ($6.894 \times 10^7 \text{ N/m}^2$) pulling pressure. In general, we would regard a film as "tightly adhering" if it could withstand in excess of $5 \times 10^7 \text{ N/m}^2$ pulling pressure, although at least $6.894 \times 10^7 \text{ N/m}^2$ is preferred. The films of the present invention are also very strong in shear stress. A Sebastian pulling post can be pulled through twenty degrees on removal of the film of the present invention.

In addition to coating flat substrates, the process of the present invention may produce coatings over curved or irregular surfaces as well. Coated surfaces of this type would be highly valuable on curved lenses, on nose-cones, on aircraft canopies and on windows. The films of the present invention have a high degree of lubricity as well as hardness and durability. The diamond-like coatings of the present invention may have superior optical, electrical, electronic, thermal and mechanical properties.

The process of the present invention utilizes the cracking of fluorocarbons as well as of hydrocarbons to produce a plasma in which radicals are generated and propelled onto a surface to produce a diamond-like coating. This coating has properties reminiscent of both diamond as well as of fluorocarbons. The coating is very hard carbon and is self lubricating in nature, probably because of polyfluorocarbon species formed in the coating. A precursor gas such as a hydrocarbon, for example methane, ethane, propane, ethylene, acetylene or similar hydrocarbon gases and vapours may be used as the precursor for the diamond-like coating. If desired, at least some of the hydrocarbon gas may be replaced by a fluorocarbon gas. This gas is cracked by intense heat to form a variety of high energy fragments, ions, radicals and free electrons

which are propelled toward the substrate and deposited thereon. Cracking to break the hydrocarbon gas or vapour into these fragments is achieved by subjecting the hydrocarbon to intense laser pulses, for example, to a CO_2 laser having a 50 nanosecond spike and a power output of 10^{14} watts/cm².

This laser impulse is absorbed by an initiator which is mixed with the hydrocarbon gas or vapour. The initiator is preferably a compound which is strongly absorbing at the output wave length of the laser impulse used. The output wave length of a ruby laser is 6943 angstroms and a helium-neon laser output wave length is 6328 angstroms, for example. The output wave length for a CO_2 laser is $10.6 \mu\text{m}$. We have found that sulfur hexafluoride is a highly effective initiator, when used with a CO_2 laser, providing both sulfur and fluoride ions and radicals on detonation. The sulfur and fluoride ions react variously with hydrocarbon and carbon species formed on detonation. Due to the high infrared irradiance levels and the presence of the highly absorbant molecule SF_6 (sulfur hexafluoride), which is strongly attenuating at $10.6 \mu\text{m}$ wave length (the output of the CO_2 laser), a high amount of laser energy is rapidly accumulated in a very small volume and is released explosively, fragmenting the hydrocarbon into highly reactive ions and radicals and imparting a high translational energy of from ten to 100 electron volts to the formed gases. The detonation produces a plasma from the gas mixture and generates a high energy detonation wave in the plasma. The presence of a plasma propagating gas, such as nitrogen or air, also aids in propagating the detonation wave and plasma generation throughout the entire volume of the mixture. The ejected carbon, hydrocarbon or other fragments and electrons receive the required transient energy from the plasma to create diamond-like materials.

Moreover, it is believed that the detonation wave produces a shower of electrons which pre-sputters the substrate, locally heating it and preparing the surface for the later arriving depositing species so that a very high adhesion of the coating to the substrate is achieved. It is believed that the tremendous surge of energy produced in the pressure wave on detonation produces an effective local temperature of thousands of degrees at the substrate and pressure in the range of thousands of kilobars. The duration of these transients of temperature and pressure is quite small, but they are effective to produce the diamond-like species of the present invention from the precursor hydrocarbon gas, to propel the species onto the substrate surface and to produce a tightly adhering bond between the diamond-like structure and the substrate.

In the accompanying drawings:

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EP 0 384 772 A1

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Figure 1 is a schematic diagram of apparatus for performing the laser deposition process of the present invention;

Figure 2 is a second schematic diagram of the apparatus of Figure 1; and

Figure 3 is a partial cross sectional view of a coated substrate.

The schematic views of Figures 1 and 2 show an apparatus 10 for producing diamond-like coatings by the process of the present invention. The apparatus 10 includes a machined aluminium box 12, which has a window 14 and gasports 16, 18 and 20 which permit the box 12 to be filled with mixtures of appropriate gases, e.g. sulfur hexafluoride, methane and nitrogen, from tanks 22, 24 and 26. A two joule pulsed CO₂ laser beam 28 (10 Hz cycle at 10.6 μ m) is transmitted into the box 12 through the infrared transmissive window 14 which may be ZnS or ZnSe. A one inch (2.54 cm) focal length, for example, in a ZnSe lens 27 assures enough gain to initiate the detonation of the gaseous mixture by the laser beam 28.

Prior to initiating deposition, a helium-neon laser 30 was used to designate a strike zone on the glass substrate 32. The CO₂ laser 34 was then fired along the helium-neon path into the plasma cell 12. A photon drag detector 36 was used to monitor the CO₂ laser pulse characteristics and a silicon photodiode 38 which was placed just behind the test cell, as shown, was used to register the emissions from the plasma. The detectors 36 and 38 were linked to a recorder 40, as shown. The apparatus 10 was also provided with a thermocouple 42 and a pressure sensor 44 and with a pump 46 and a residual gas analysis unit 48, as shown. The air in the box 12 was evacuated to about ten torr (1333 Pa) and the box 12 was backfilled with SF₆ at sixty torr (7999 Pa) and CH₄ at 100 torr (13330 Pa). The gas was then detonated as described above.

Deposition of diamond-like material occurs over the entire interior 36 of box 12. The character of the material deposited varies with the distance from the plasma sheath. Deposits adjacent to the plasma on the infrared window 14 were smooth, continuous and between about five to ten μ m in thickness. The deposits on the infrared window 14 were extremely hard and tightly adhering and had superior optical properties. The depth of the deposits on the infrared window 14 may be tuned to increase or decrease the diamond-like character and conversely increase or decrease the fluorocarbon-like character by adjustment of the focus of the laser beam 28 toward or away from the substrate 32. Deposits occurring on the substrate 32, the rear glass window, were considerably thicker and more granular than those occurring on the infrared window 14, yet were similar in composition and were tightly adher-

ing. The materials on window 32 were quite satisfactory as an abrasive surface.

Analysis of the coatings found in the box 12 indicated a very hard, fluorocarbon containing, diamond-like material having a tight bond to the substrate 32 and window 14. Substantial hand pressure was required with a steel spatula to remove the granular material from the glass substrate 32. The coating on the ZnSe lens, window 14, was also very hard and tightly bonding and suitable to protect the window 14 from rain and/or ice erosion. Rain and ice are a problem for infrared windows, such as the infrared lenses used on weather cameras, which are typically made from soft material. In addition, the smooth coatings appeared to have very high lubricating properties and would be suitable for parts subject to sliding friction such as valves, pistons and bearings. As noted above, the larger grained deposits appeared to be excellent as abrasive coatings. They would be suitable on grinding wheels or blades or on glass or metal substrates. The adhesion of the coatings was very high and the material was sufficiently hard to scratch glass. The thin, smooth diamond-like coating appeared to have sufficient hardness and suitable electrical properties that it could be used as a microelectronic substrate, for example, as a substrate for electronic circuitry prepared by photolithographic processes.

As shown in Figure 3, the diamond-like coating 50 is formed as a hard, tightly adhering coating on substrate 14, the infrared window. The diamond-like coating 50 has a thickness of about ten μ m. As so coated, infrared window 14 would be suitable for use as an infrared window or lens subject to erosion from exposure to ice, rain and other abrasive environments. While Figure 3 shows the substrate as being the infrared window 14, it will be appreciated that glass substrate 32, or metal or any other substrate material can be used.

Claims

1. A substrate having a hard diamond-like coating thereon, the diamond-like coating being tightly bonded to the substrate and containing fluorocarbon moieties.

2. A substrate according to Claim 1, in which the diamond-like coating has a smooth, non-scattering optically transparent surface and the coated substrate is an optical element.

3. A substrate according to Claim 1, in which the coated substrate is a wear resistant friction bearing surface.

4. A substrate according to Claim 1, in which the coated substrate is an abrasive element.

5. A method of producing a diamond-like coat-

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EP 0 384 772 A1

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ing, which comprises introducing a laser generated beam into a confined hydrocarbon-containing precursor gas to initiate a plasma in the precursor gas and create diamond-like precursor fragments from the precursor gas, the plasma propelling the fragments onto a substrate and bonding the fragments to the substrate as a diamond-like coating.

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6. A method according to Claim 5, in which the precursor gas is confined at a pressure of up to one atmosphere.

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7. A method according to Claim 5 or Claim 6, in which the laser beam is generated by a CO₂ laser.

8. A method according to any one of Claims 5 to 7, in which the precursor gas contains a plasma initiator.

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9. A method according to Claim 8, in which the plasma initiator is a gas which strongly absorbs in the wave length of the laser generated beam.

10. A method according to any one of Claims 5 to 9, in which the plasma initiator is sulfur hexafluoride.

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11. A method according to any one of Claims 5 to 10, in which the precursor gas contains a plasma propagating gas.

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12. A method according to Claim 11, in which the plasma propagating gas is nitrogen.

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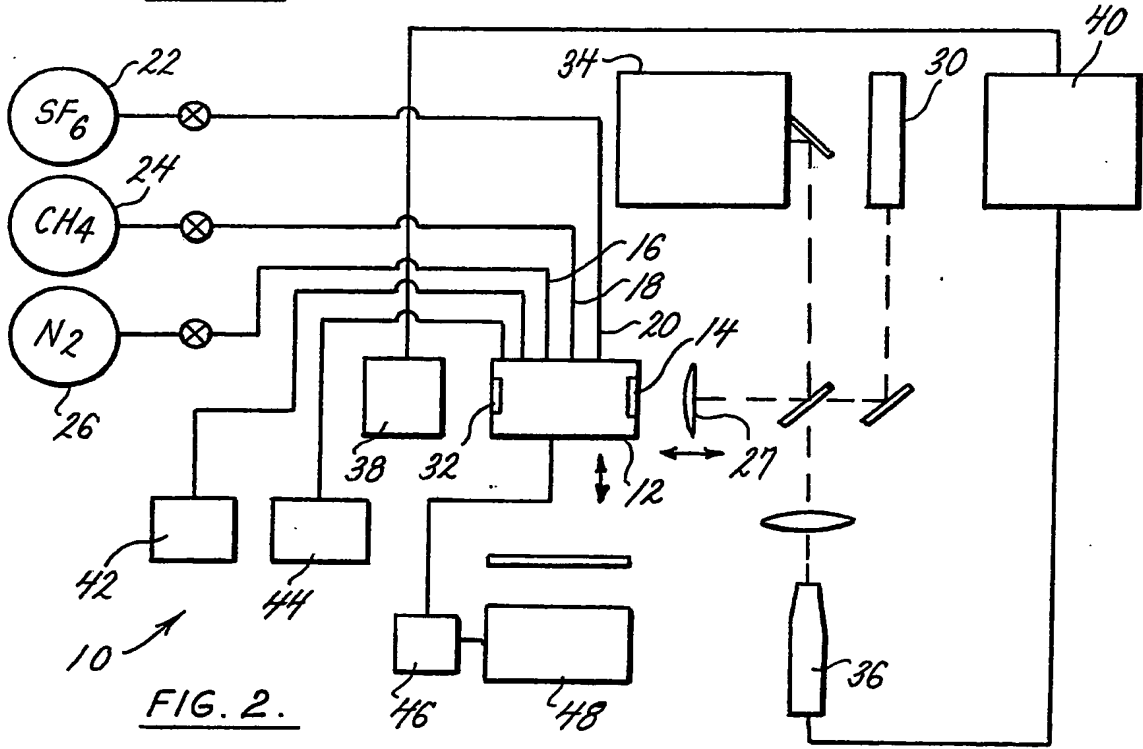
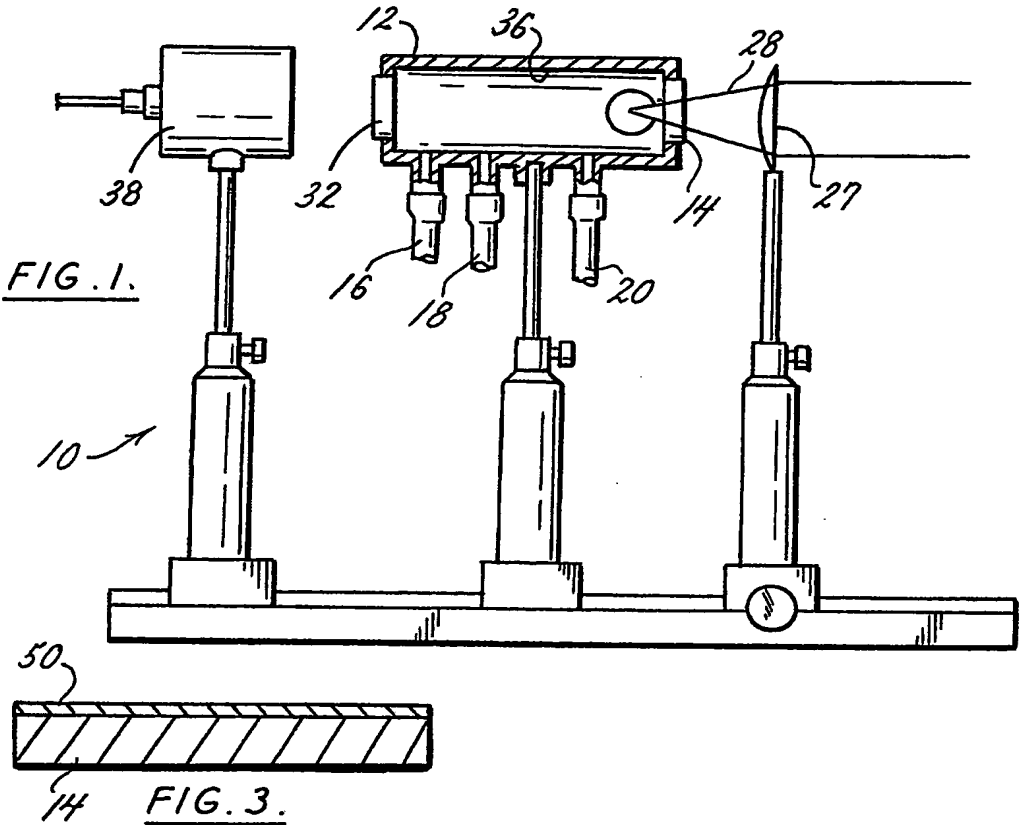
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EP 0 384 772 A1





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EUROPEAN SEARCH REPORT

Application number

DOCUMENTS CONSIDERED TO BE RELEVANT			EP 90301956.0
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.)
Y	EP - A2 - 0 175 980 (ENERGY CONVERSION DEV.) * Claims 1,9 *	1	C 23 C 16/26 C 23 C 16/48 C 01 B 31/00
Y	EP - A1 - 0 206 603 (MORRISON PUMPS) * Claim 1; page 5, lines 12-16 *	1	
A	EP - A2 - 0 288 065 (IDEMITSU PETROCHEMICAL) * Claims 1,4 *	1	
			TECHNICAL FIELDS SEARCHED (Int. Cl.)
			C 23 C C 01 B
The present search report has been drawn up for all claims			
Place of search		Date of completion of the search	Examiner
VIENNA		11-05-1990	MARCHART
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

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